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13. ABSTRACT *(Maximum 200 words)*

We have developed synthetic schemes which allow the synthesis of graft copolymers with precisely controlled architectures and narrow molecular weight distributions. The study of the properties of these materials, through collaborations with Professor Samuel Gido (Univ. Of Massachusetts) and others, has led to an enhanced understanding of the effect of branching on block copolymer morphology. Flexible/semi-rigid block copolymers have also been synthesized and studied in order to explore effects of chain stiffness on block copolymers. The results from these studies are summarized herein; details are given in the fifteen refereed publications that have been produced during this project.

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List of All Participating Scientific Personnel Showing Any Advanced Degrees Earned by Them While Employed on the Project

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Statement of the Problem Studied

While linear flexible/flexible diblock and triblock copolymers have been studied for many years, relatively few investigations have probed the effects of branching and chain stiffness on the properties of these materials. This has been largely due to the fact that well-defined, well-characterized materials of this type had been unavailable prior to the present work. The goal of this work was to synthesize graft and flexible/semi-rigid block copolymers having precisely controlled structures, to thoroughly characterize these materials, and to study their morphological properties in collaboration with the group of Professor Samuel Gido (University of Massachusetts).

Summary of the Most Important Results

1) Through the use of high vacuum anionic polymerization and controlled chlorosilane linking chemistry, we have developed methods which allow precise control over branch number and branch placement in graft copolymers. This chemistry (which takes advantage of stable anions, reactions with chlorosilanes which are free of side reactions, and steric effects during linking) is a new mechanism for graft copolymers formation which is superior to other techniques in terms of architectural control. These synthetic methods allow for rigorous characterization of the architecture, compositions, and molecular weights of these materials. With this chemistry we have synthesized:

- "simple grafts" which have a single centrally located branch point
- "asymmetric simple grafts" which have a single branch point placed off-center at a predetermined position.
- "π copolymers" which have two branch points that are equally spaced along the backbone.
- "H copolymers" which have a branch point at each end of the backbone and the "grafts" are attached at their midpoints.
- "centipedes" which have multiple, regularly spaced branch points with two "grafts" attached at each branch point.
- "combs" which have multiple, regularly spaced branch points with one "graft" attached at each branch point.

All of these materials, based on polystyrene and polyisoprene, can be produced with virtually any desired composition and molecular weight, as well as with very narrow molecular weight distributions.

2) The morphological characteristics of the graft copolymers described above have been investigated in collaboration with the group of Professor Sam Gido (Univ. Of Massachusetts) and others. For the "simple grafts", a direct comparison with theoretical predictions by Dr. Scott Milner (Exxon) on the effect of branching on block copolymer morphology has been conducted. The morphologies of six of the samples correspond to classical phases (spheres, cylinders, lamellae) and are in agreement with predictions of Milner. This is an important finding because this

means that by introducing branching in block copolymers, one can decouple the morphology from a strict dependence on copolymer composition. Furthermore, we have found that the degree of long range order in microphase separated block copolymers is strongly influenced by branching. This has important implications for the production of copolymer-based membranes.

3) For the 7th simple graft copolymer, which has a composition near a "bicontinuous window" predicted by Milner, a new morphology was discovered. This morphology, which was featured as the cover art for the journal Macromolecules during all of 1997, is a randomly-oriented wormlike (ROW) morphology, which had never before been observed in neat block copolymer systems. The equillibrium nature of this micellar ROW morphology was confirmed by selective solvent casting/annealing experiments.

4) We have synthesized and characterized two series of conformationaly asymmetric diblock copolymers: polyisoprene/poly(tert-butylmethacrylate)(PI/PtBMA) and poly(styrene)/poly(cyclohexadiene) (PS/PCHD). PI/PtBMA exhibits only a modest degree of conformational asymmetry, yet a shifting of the phase diagram, similar to that observed for the grafts, was noted. Furthermore, these systems showed that chain stiffness, as well as branching, could be used to manipulate long range order in block copolymers. With the PS/PCHD materials, the conformational asymmetry is more pronounced. With these materials we and our collaborators have discovered a very unusual "cylinders-within cylinders" morphology.

List of All Publications Acknowledging Support of this Grant

1. "End-Functionalized Block Copolymers of Styrene and Isoprene. A DSC Study", S. Pispas, N. Hadjichristidis, and J. W. Mays, Polymer, 37, 3989-91 (1996).

2. "Micellization of ω-Functionalized Poly(styrene-b-isoprene) Copolymers in n-Decane)", S. Pispas, S. Allorio, N. Hadjichristidis, and J. W. Mays, Macromolecules, 29, 2903-08 (1996).

3. "Bulk Morphologies of Microphase Separated A_2B Simple Graft Block Copolymers", D. J. Pochan, S. P. Gido, S. Pispas, J. W. Mays, A. J. Ryan, P. Fairclough, N. Terrill, and I. W. Hamley, Macromolecules, 29, 5091-5098 (1996).

4. "Synthesis, Characterization, and Morphology of Model Graft Copolymers with Trifunctional Branch Points", S. Pispas, J. W. Mays, D. Pochan, S. P. Gido, and N. Hadjichristidis, Macromolecules, 29, 7022-28 (1996).

5. "Morphological Transition in an I_2S Simple Graft Block Copolymer: From Folded Sheets to Folded Lace to Randomly Oriented Worms at Equilibrium", D. J. Pochan, S. P. Gido, S. Pispas, and J. W. Mays, Macromolecules, 29, 5099-5105, (1996).

6. "Morphologies of Microphase Separated Conformationally Asymmetric Diblock

Copolymers", D. J. Pochan, S. P. Gido, J. Zhou, J. W. Mays, M. Whitmore, and A. J. Ryan, J. Polym. Sci., Polym. Phys. Ed., 35, 2629-43 (1997).

7. "Non-Linear Block Copolymer Architectures", M. Pitsikalis, S. Pispas, J. W. Mays, and N. Hadjichristidis, invited review for Adv. Polym. Sci., 135, 1-137 (1998).

8. "Micellization of Model Graft Copolymers of the H and π Type in Dilute Solution", S. Pispas, N. Hadjichristidis, and J. W. Mays, Macromolecules, 29, 7378-7385 (1996).

9. "Self-Diffusivity in Block Copolymer Solutions: 2. A_2B Simple Grafts", S. H. Anastasiadis, K. Chrissopoulou, G. Fytas, G. Fleisher, S. Pispas, M. Pitsikalis, J. W. Mays, and N. Hadjichristidis, Macromolecules, 30, 2445-2453, (1997).

10. "Asymmetric Single Graft Block Copolymers: Effect of Molecular Architecture on Morphology", C. Lee, S. P. Gido, M. Pitsikalis, J. W. Mays, N. Beck Tan, S. Trevino, and N. Hadjichristidis, Macromolecules, 30, 3732-3738 (1997).

11. "$H(S_2IS_2)$ Block Copolymers: Effect of Molecular Architecture on Morphology", C. Lee, S. P. Gido, Y. Poulos, N. Hadjichristidis, N. Beck Tan, S. F. Trevino, and J. W. Mays, J. Chem. Phys., 107, 6460-69 (1997).

12. "Micellization of Model Graft Copolymers in Dilute Solution", M. Pitsikalis, J. Woodward, J. W. Mays, and N. Hadjichristidis, Macromolecules, 30, 5384-5389, (1997).

13. "π-Shaped Double Graft Copolymers: Effect of Molecular Architecture on Morphology", C. Lee, S. P. Gido, Y. Poulos, N. Hadjichristidis, N. B. Tan, S. F. Trevino, and J. W. Mays, Polymer, in press.

14. "Synthesis and Characterization of Regular Multigraft PS Homopolymers (Homocentipedes) and Pi/PS Copolymers (Co-Centipedes) with Double Polystyrene Branches. Effect of sec-BuOLi on the Polymerization of Isoprene with (1,3-phenylene)-bis-(3-methyl-1-phenylpentylidene) Dilithium Initiator", H. Iatrou, J.W.Mays, and N. Hadjichristidis, Macromolecules, submitted (1998).

15. "Linking Reaction of Living Polymers with Bromomethylbenzene Derivatives. Synthesis and Characterization of Star Homopolymers and Graft Copolymers with Polyelectrolyte Branches", M. Pitsikalis, S. Sioula, S. Pispas, N. Hadjichristidis, D. C. Cook, J. Li, and J.W. Mays, Designed Monomers and Polymers, submitted (1998).

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